

STRUCTURAL INFORMATION FROM THE SELECTIVE METHYLATION OF ACIDIC O-H AND C-H
SITES IN AN ARGONNE PREMIUM COAL SAMPLE*

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INTRODUCTION

With the establishment of the Argonne Premium Coal Sample Program (1), a long-term supply of a limited number of coal samples for basic research has become available to the coal research community. These coals offer the advantage of having been processed and stored under the controlled conditions of relative humidity, temperature, minimum oxygen exposure, etc. Since special care has been taken to insure sample homogeneity, direct inter-laboratory comparisons of experimental results will now be possible. Furthermore, it will now be possible to evaluate the chemical and physical changes which accompany the long-term storage of coal.

RESULTS AND DISCUSSION

Initially, it will be necessary to fully characterize the physical and chemical properties of these samples by a variety of chemical and spectroscopic means. It has been demonstrated that important coal structural information can be established by the application of selective chemical modification reactions to derivatize independently the acidic O-H and C-H sites in coal. For example, it is possible to O-alkylate the phenols and carboxylic acids in bituminous and sub-bituminous coals by reaction with hydroxide and methyl iodide (2) or methyl tosylate (3). Solid (2c,4) and solution (2b) ^{13}C NMR of coal derivatives prepared with C-13 enriched methylating agents have established that indeed O-methylation of phenols and carboxylic acids does occur. On the other hand, it is apparent that significant C-alkylation also occurs under the phase-transfer O-alkylation procedure developed by Liotta (2). For example, as much as 30% of the chemistry is C-alkylation when Illinois No. 6 hvCb is the coal and the alkylation conditions are tetrabutylammonium hydroxide (TBAH) and methyl iodide in aqueous THF (4). The reasons for this phenomenon have never been established. It could derive from ionization and methylation of highly acidic C-H sites or it may indicate competitive O- and C-methylation of phenoxide salts (5). Whatever the reason(s), the results clearly demonstrate that a 'fine tuning' of the reaction conditions towards exclusive O-alkylation is desirable.

We have found that it is possible to 'fine tune' this O-methylation reaction in favor of carboxyl vs phenolic O-methylation by limiting the amount of hydroxide base and replacing the methyl iodide or methyl tosylate with dimethyl sulfate (6). Specifically, the coal is treated with an excess of TBAH. After a specified time

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period (16 h), the excess base is neutralized with HCl. This 'back titration' with acid is monitored, a glass electrode being used to evaluate the pH of the solution. After equilibration, the resulting coal anions are quenched with C-13, C-14 double labelled dimethyl sulfate. The pH dependency of the reaction is evaluated by measuring the total number of introduced methyl groups using C-14 combustion analysis (7). The number of methyl esters in the alkylated coals is defined as the number of hydroxide labile methyl groups measured by hydrolysis (8). Typical results are shown in Table 1 for a nonpremium sample of Illinois No. 6 hvCb. As expected, the degree of methylation is a sensitive function of the solution pH. Over the pH region 2-12, the total number of added methyls increases with an increase in solution pH. More importantly, however, is the observation that the formation of methyl esters is preferred at the lower pH values ($\text{pH} < 7$). This useful property of coal means that the reaction selectivity can be optimized by careful control of the reaction pH. The 'site specificity' of the reaction can be evaluated quantitatively by measuring the ratio, base labile methyls to total methyls. For this particular coal sample, site specificities approaching 70% can be realized when the methylation is carried out at pH 2-7.

An important step in the selective methylation of the acidic C-H sites in coal is the conversion of the phenols and carboxylic acids to their methyl ether and methyl ester derivatives (6,8,9). This is accomplished by the preparation of a pH 12 O-methyl coal using natural abundance dimethyl sulfate as the methylating agent.

To examine the distribution of acidic C-H sites in coal by selective C-methylation chemistry, the pH 12 O-methyl coal is treated in separate experiments with an excess of the conjugate bases of 9-phenylfluorene ($\text{pK}_a = 19$ in THF (10)), fluorene ($\text{pK}_a = 22$ in THF (10)) and triphenylmethane ($\text{pK}_a = 31$ in THF (10)) as their lithium salts (solvent:THF, T:0°C). After a predetermined neutralization time (68 h, typically), the reaction mixtures are quenched with C-13, C-14 double labelled methyl iodide and the products isolated by a series of organic and aqueous extractions. ^{14}C combustion analysis is used to establish the number of $^{14}\text{CH}_3$ groups introduced under each set of reaction conditions. The isolated derivatives are treated sequentially with base and $^{13,14}\text{CH}_3\text{I}$ a total of three times. Previous work (6,9) has established that repetitive treatments are necessary to achieve exhaustive C-methylation. This observation along with the CP/MAS ^{13}C NMR of serially alkylated coal derivatives suggest the chemistry includes the reaction of structural units containing the $-\text{CH}_2-$ group (11).

To facilitate the discussion of the results, we define the number of acidic C-H sites with $\text{pK}_a < 19$ as equal to the number of $^{14}\text{CH}_3$ groups introduced when 9-phenylfluorenyllithium is the base. The number of acidic C-H sites with $19 < \text{pK}_a < 22$ is taken as the difference: number of $^{14}\text{CH}_3$ added with fluorenyllithium minus the number of $^{14}\text{CH}_3$ added with 9-phenylfluorenyllithium. And finally, the number of acidic C-H sites with $22 < \text{pK}_a < 31$ is set equivalent to the difference: number of $^{14}\text{CH}_3$ added with trityllithium minus the number of $^{14}\text{CH}_3$ added with fluorenyllithium.

The structural information available from the application of this chemical approach is illustrated in Table 2 for an O-methyl low volatile bituminous coal, PSOC 1197 (6). Specifically, we can evaluate the distribution of acidic C-H sites in coal as a function of pK_a . In terms of coal structure analysis, this type of information is particularly useful. Since the pK_a values for C-H groups in a variety of organic compounds have been evaluated (10), we can begin to assign a structure to the reactive structural units. For this particular coal, namely

PSOC 1197, we note that the majority of the C-H sites have pK_a values $19 < pK_a < 22$. This observation suggests that structural types such as indenenes and fluorenes as well as those containing C-H bonds adjacent to electron withdrawing substituents (e.g., carbonyl) are important structural features in this bituminous coal, while 9,10-dihydroanthracene structural types are absent. The results from the application of these structural probes to one of the coals from the Argonne Premium Coal Sample Program will be presented during the talk.

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Table 1. Selective O-Methylation of Illinois No. 6 using $n\text{Bu}_4\text{NOH}$ and $^{13,14}(\text{CH}_3)_2\text{SO}_4$

pH	No. $^{14}\text{CH}_3/100$ Coal C		Site Specificity
	Total	Base Labile	
12	4.0 ± 0.4	1.1 ± 0.1	$28 \pm 5\%$
7	1.37 ± 0.01	0.90 ± 0.01	$66 \pm 1\%$
5	0.90 ± 0.08	0.68 ± 0.05	$76 \pm 13\%$
2	0.18 ± 0.02	0.12 ± 0.01	$66 \pm 14\%$

Table 2. Selective C-Methylation of O-Methyl PSOC 1197: The Distribution of Acidic C-H Sites as a Function of pK_a

pK_a Range	No. C-H Sites/100 Coal C
$\text{pK}_a < 19$	0.06
$19 < \text{pK}_a < 22$	1.8
$22 < \text{pK}_a < 31$	0